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Method for coating the surface of a metal material, device for carrying out the method and product obtained in this manner

The invention relates to the coating of metal surfaces. More precisely, it relates to processing operations for coating the surface of a metal material intended to confer a three-dimensional visual effect on the material.

A visual effect of this type can be achieved using holograms which are produced by recording and reproducing an image by means of two laser beams on a photosensitive medium which is capable of recording highly contrasting luminous interferences. Media of this type are, for example, thermoplastic films, photopolymers, photosensitive films…

Up to the present time, in order to produce a three-dimensional visual effect on a metal surface, no method has been known other than to apply to the surface, by means of adhesive-bonding or colamination, a photosensitive medium of the type described above. The decoration of metal packagings of steel or aluminium is a preferred use of this technique which has the disadvantage for the metal company of requiring the involvement of an external supplier to provide the photosensitive medium. Furthermore, there is the risk of the medium becoming separated from the packaging or damaged during processing and handling operations to which the packaging is subjected following the adhesive-bonding or colamination.

The object of the invention is to provide a method which allows three-dimensional visual effects to be produced on the

surface of a metal material without a photosensitive medium having to be applied to the surface.

To this end, the subject-matter of the invention is a method for coating the surface of a metal material having a crystallographic structure, according to which the material is first coated with a layer of a metal or a metal alloy having a melting point equal to T_f and a thickness less than or equal to 2.5µm, characterised in that:

- the first coating is subjected to thermal processing using a rapid heating means in order to bring the surface of the first coating to a temperature of between $0.8T_f$ and T_f;
- a second coating is deposited from a metal or a metal alloy having a thickness less than or equal to 1µm.

According to a variant of the method, the first and second coatings have melting points less than or equal to 700°C.

The first and second coatings can be constituted by the same material.

According to a variant of the method, a transparent mineral film is then deposited on the second coating.

The metal material to be coated can preferably be a carbon steel, a stainless steel, or aluminium or one of the alloys thereof.

The first coating can preferably be produced by means of electrodeposition or a physical vapour deposition method.

The rapid heating means can preferably be an infra-red heating device, an induction heating device, a device for

discharge with plasma with a non-reactive gas or a device for ion bombardment with a non-reactive gas.

The second coating can preferably be produced by means of electrodeposition or a physical vapour deposition method.

The transparent mineral film can be deposited by means of a reactive plasma assisted chemical vapour deposition method.

The first and second coatings can each be constituted by tin and/or aluminium.

The mineral film can be constituted by a metal oxide or a mixture of metal oxides, preferably selected from the oxides of austenitic stainless steel, chromium, titanium, silicon, zinc, tin.

The metal material can be in the form of a moving strip and the various method steps can be carried out continuously by means of installations which are arranged successively over the path of the moving strip.

The invention also relates to a device for coating a metal material in the form of a strip, characterised in that it comprises means for moving the strip and, arranged successively over the path of the strip:

- first means for coating the strip with a layer of a metal or a metal alloy having a melting point equal to T_f;
- means for rapidly heating the strip which can bring the surface of the layer to a temperature of between $0.8T_f$ and T_f; and

- second means for coating the strip with a layer of metal or metal alloy.

The device can comprise, downstream of the second means for coating the strip with a layer of a metal or a metal alloy, means for coating the strip with a transparent mineral film.

The invention also relates to a metal material, characterised in that it comprises, on at least one of the surfaces thereof, a metal coating which has a three-dimensional visual effect, the coating being formed directly on the surface of the material, and which is carried out in particular by the above method.

As will be appreciated, the invention consists in producing the desired three-dimensional visual effect using a series of operations for processing the surface of the metal material itself. In this manner, a multilayered coating is produced which cannot be separated from the metal material and which can be produced by the metal company which made the base material. This coating, in addition to the aesthetic qualities thereof, has a number of technical advantages and allows the manufacturer of the metal material to maintain complete control over the decoration process.

The invention will be better understood from a reading of the following description, given with reference to appended Figures 1 to 6 which illustrate the appearances of various coatings produced by different variants of the method according to the invention.

The starting material is a metal material, such as a carbon steel, a stainless steel, aluminium or one of the alloys

thereof, etcetera. It is, for example, in the form of a plate or a wound strip. In this last case, it is possible to carry out the processing operation which will be described by unwinding the strip and moving it continuously in an installation where the equipment which allows the various steps of the processing operation to be carried out is arranged successively over the path of the strip. In order to achieve the desired aesthetic effect, it is necessary for the metal material used as a substrate to have a crystallographic structure.

Before carrying out the depositing, the surface of the material is conditioned in a manner known per se in order to remove any superficial contamination.

The first method step is the depositing of a first coating, constituted by a metal element (tin or aluminium, for example) or a metal alloy, preferably having a low melting point T_f in the order of 700ºC or less. This coating must have a thickness less than or equal to 2.5μm.

Advantageously, it is produced by means of an electrodeposition method or a physical vapour deposition method. The physical vapour deposition methods which can be used include conventionally known methods involving vacuum evaporation, magnetron sputtering, ion plating, self-induced ion plating.

The second method step is a thermal processing operation which is carried out on the first coating using a rapid heating means, such as infra-red lamps, an inductor, a plasma discharge operation, or ion bombardment with a non-reactive gas, such as an inert gas. This thermal processing must bring

the surface of the first coating to a temperature of between 0.8 T_f and T_f. So that it is effected with kinetics compatible with being carried out on a strip moving at a speed in the order of 100m/mn, it is preferable for T_f to be less than or equal to 700ºC.

The third method step is the depositing of a second coating, from a metal element or an alloy which may or may not be identical to the material of the first coating. This coating must have a thickness which does not exceed 1μm. It can be produced using the same methods as the first coating.

Preferably (but not necessarily), the method can comprise a fourth step which consists in depositing a transparent mineral film on the second metal coating. Materials such as oxides of austenitic stainless steel, chromium, titanium, silicon, zinc, tin (non-limiting list) and the mixtures thereof are particularly appropriate. This transparent mineral deposit can be carried out by any known means for this purpose, the reactive plasma assisted chemical vapour deposition methods being particularly appropriate. If this film has a thickness less than or equal to 1μm, a coloured coating can be produced by means of an interference effect of the mineral film. The colours green, yellow, blue, violet and red are accessible in this manner, in accordance with the refraction index of the material deposited. Generally, this transparent film gives an appearance of additional depth to patterns having a three-dimensional appearance which are produced following the first three method steps.

As mentioned, the appearance of patterns on the surface of the substrate requires the substrate to have a crystallographic structure. The nucleation of the

solidification patterns of the metal deposits is produced on the basis of preferential sites at the surface of the substrate which exist only if the substrate has a crystallographic structure.

The size of the patterns produced depends on the quantity of energy used during the second method step and the thickness of the coating: the patterns will be larger as this quantity of energy and/or this thickness become(s) greater. The use of a metal or alloy having a low melting point (700ºC or less) as a coating material during the first method step allows the metallurgical conversion of the coating to be carried out in a very short space of time during the second step. The methods of heating which have been mentioned allow the necessary energy to be provided in the shortest possible time.

Compared with producing three-dimensional visual effects using photosensitive media applied to the metal product, the method according to the invention has a number of advantages. As mentioned, it allows the manufacturer of metal products to maintain complete control over the method. Since the coating which produces the three-dimensional visual effect is an integral part of the medium in this case, there is no risk of it becoming separated during subsequent processing and handling operations. Furthermore, most particularly if the method is used in its entirety with four steps, the coating produced in this manner increases the resistance of the substrate to cosmetic corrosion. The coating also has a higher resistance to ultra-violet radiation and temperature. It is less sensitive to fingermarks. It has a high degree of superficial hardness which makes it less sensitive to scratches. It is easy to clean and effectively withstands maintenance products and other mechanical influences. Finally,

it is possible, if the coating metal used is appropriate (for example, tin), to make the coating compatible with use in the field of foodstuffs.

Various examples for carrying out the method according to the invention will now be described. They are carried out on sheets of soft steel of 200 x 200mm and a thickness of 0.7mm. These sheets are degreased beforehand in conventional manner using damp means (solvent agitated by ultrasound). They are then subjected to an ion pickling operation starting from an argon plasma in a vacuum reactor which is then used during the various steps for carrying out the method according to the invention.

Example 1

In the first method step according to the invention, the sheet is coated with a layer of tin of 0.8μm by means of magnetron sputtering in an atmosphere of argon at a pressure of 10^{-3}mbar (0.1Pa). The target current is 0.9A and the target voltage is 450V. The rate at which the tin is deposited is 0.25μm/min.

In the second method step according to the invention, the sheet is thermally processed using an argon plasma at a pressure of 10^{-3}mbar (0.1Pa). The energy conferred on the ions of argon is 400eV and the quantity of ions received by the sheet is 4.7×10^{22} ions Ar^+/m^2. The sheet is placed as a cathode. The surface of the tin is brought to a temperature in the order of 210ºC.

In the third step, a tin coating of 0.4μm is deposited by means of magnetron sputtering, under the same experimental conditions as for the first coating.

In the fourth step, a transparent film of silicon having a thickness of 0.1μm is deposited by means of plasma CVD. The depositing is carried out in an atmosphere composed of hexamethyldisiloxane (HMDSO) and oxygen at a pressure of 10^{-3}mbar (0.1Pa), with a ratio of partial pressures of HMDSO and O_2 of 1/10. A current is used having a frequency of 50kHz at a power of 100W. The depositing rate is 1.0μm/min.

Using this method, a coating is produced whose external appearance is illustrated in Figure 1, which coating has anti-corrosion and anti-fingermarking properties, is easy to clean and has a high degree of superficial hardness. It is capable of withstanding significant mechanical, chemical and thermal influences.

Example 2

The sheet of steel is coated under conditions identical to those of example 1 for the first three steps. The fourth step consists in producing a coloured film of titanium dioxide by means of reactive magnetron sputtering of a titanium target. The thickness of the film is 0.05μm. The conditions under which it is produced are an atmosphere O_2/Ar with P_{O2}/P_{Ar} = 0.4, a total pressure of 5.10^{-3}mbar (10.5Pa) and a power of 1.7kW. In this manner, a coating is produced which is illustrated in Figure 2, having properties similar to those of example 1, additionally with a blue appearance owing to the refraction index of the titanium dioxide (2.5) and the properties specific to titanium dioxide, that is to say, significant chemical inertia, a high degree of stability at high temperature, effective resistance to chemical influences and a self-cleaning action owing to the catalytic effect

thereof of degradation of the materials containing carbon and oxygen in the presence of ultra-violet light.

Example 3

The sheet of soft steel is coated under the same conditions as for example 2, with the exception that the thickness of the first deposit of tin is increased to 1.2μm, and the quantity of ions received by the first layer of tin during the second method step is increased. In this case, this quantity reaches 9.4×10^{22} ions Ar^+/m^2. The surface of the tin is brought to a temperature in the order of 235ºC. The result can be seen in Figure 3.

Example 4

The sheet of soft steel is coated under the same conditions as for example 2, with the exception that, as for example 3, the quantity of ions received by the first layer is increased to 9.4×10^{22} ions Ar^+/m^2, and the thickness of the titanium dioxide film is increased to 0.08μm. The result can be seen in Figure 4.

It should be noted that the increase in the energy used during the second processing step leads to a significant increase in the size of the patterns.

Example 5

The sheet is coated under identical conditions to those of example 1, with the exception that, for the second step, two infra-red lamps are used to heat the substrate and the first layer of tin thereof, and no oxide is deposited on the second

layer of tin. Only the first three method steps are therefore carried out, those which are required to produce the desired three-dimensional visual effect. The heating of the layer of tin is static and lasts for 8 minutes in a lamp-type furnace controlled at a temperature of 200ºC. The result can be seen in Figure 5.

Example 6

A very thin sheet of soft steel of 200 x 200mm and 0.2mm thick is coated with an electrodeposited layer of tin in such a manner as to produce a sheet of "tinplate" of the type conventionally used in the field of foodstuffs. The second and third method steps according to the invention are then carried out under conditions identical to those of example 2. The fourth optional processing step according to the invention is not carried out. The result can be seen in Figure 6.

Example 7

In a first method step according to the invention, the sheet is coated with a layer of aluminium of 0.6μm by means of magnetron sputtering in an atmosphere of argon at a pressure of 10^{-3}mbar (0.1Pa). The target current is 1.8A and the target voltage is 355V. The rate at which the aluminium is deposited is 0.33μm/min.

In the second method step according to the invention, the sheet is thermally processed with an argon plasma at a pressure of 10^{-3}mbar (0.1Pa). The energy conferred on the argon ions is 280eV and the quantity of ions is 18.4×10^{22} ions Ar^+/m^2. The sheet is placed as a cathode. The surface of

the sheet coated in aluminium is brought to a temperature of 615ºC at the end of the processing operation.

In a third step, a coating of tin is deposited by means of magnetron sputtering under the same experimental conditions as those described in the third step of example 1.

Under these production conditions, a coating is produced whose external appearance is identical to that of the example of Figure 1.

Example 8

The sheet of soft steel is coated with tin under the same conditions as for example 3 for the first two steps. In a third step, an aluminium coating is deposited by means of magnetron sputtering, under the same experimental conditions as those described in the first step of example 7, with the exception that the aluminium is deposited with a thickness of $0.4 \mu m$.

Under these production conditions, a coating is produced whose external appearance is identical to that of the example of Figure 3.

The examples of materials which form the substrate and the various layers which coat it, and the conditions under which they are formed have been given in a non-limiting manner. The person skilled in the art will be able to envisage variants in accordance with the desired properties of the final product.

If the three-dimensional visual appearance is desired on only one surface or portions of the surface of the metal material, it is possible to protect the material using one or more covers which mask the zones which are not to be coated during the various processing operations to which they are subjected.